Influence of the Head Group Size on the Direction of Tilt in Langmuir Monolayers

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Abstract -

A model of rods with heads of variable size, which are confined to a planar surface, is used to study the influence of the head group size on tilted phases in Langmuir monolayers. Simple free energy considerations as well as exact zero temperature calculations indicate that molecules with small head groups tilt towards next nearest neighbors, and molecules with larger head groups towards nearest neighbors. This provides a possible explanation for recent experimental results, and for details of the generic phase diagram for fatty acid monolayers.

PACS numbers: 68.18, 68.35

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1   Introduction.

Monolayers of simple amphiphiles at the air-water interface form a complex variety of condensed phases [1, 2]. A generic phase diagram for fatty acids is shown in Figure 1. The phase behavior appears to be driven mainly by the conformations of the aliphatic tails of the molecules. However, head group interactions also play a role, especially in tilted phases. Shih *et al* [3] and Fischer *et al* [4] have recently performed systematic studies of mixtures of heneicosanic acid and heneicosanol. They find that the $L_{2(h,d)}$ phases with tilt towards nearest neighbors are gradually suppressed, as the alcohols are added to the fatty acid monolayer, until they finally disappear at alcohol concentrations above 35 %. In pure heneicosanol monolayers, only phases with tilt towards next nearest neighbors exist.

According to a common picture, tilt order in monolayers is often induced by a mismatch between the head group spacing and the chain diameter. The size of the head groups plays a crucial role for this mechanism. From the observation that the zero pressure lattice constant is smaller in heneicosanol monolayers than in heneicosanic acid monolayers [3], one can deduce that the effective size of alcohol head groups in water is smaller than that of fatty acid head groups. The results of Shih *et al* and Fischer *et al* therefore suggest that the head group size also determines the direction of tilt. Further investigations of surface pressure – temperature phase diagrams for monolayers of fatty acids with esters by Teer *et al* [5] are consistent with this picture.

We investigate this possibility in the framework of the simplest possible theoretical model: Amphiphilic molecules are represented by rigid rods with heads larger than the rod diameter. We discuss the model first using a simple,

general free energy *ansatz*. Our results are confirmed by exact zero temperature calculations for a system with Lennard-Jones interactions.

2   Free Energy Considerations.

We consider rigid rods of length L with steric repulsive interactions and longer range attractive interactions; the favorite distance between two rods at given temperature is r_t. The rods have heads of radius r_h, which are confined to a planar surface and arranged on a distorted hexagonal lattice, with variable lattice constants a and b (Figure 2). Two cases are discussed, tilt in the direction of a (nearest neighbors, NN) and tilt in the direction of b (next nearest neighbors, NNN). In this geometry, rods have two different types of neighbors, labelled (i) and (ii) in the following.

The head size gives rise to the geometrical constraints

$$\text{(i)} \qquad a \geq r_h \qquad \text{(ii)} \qquad (a^2 + b^2)/4 \geq r_h^2. \tag{1}$$

If the heads are small, $r_h \leq r_t$, the optimal configuration is one of untilted rods arranged on an undistorted hexagonal lattice, with the lattice constant $a = r_t$. The volume per rod of the rod layer is then given by $V_0 = \sqrt{3}/2\, r_t^2\, L$. If the heads are larger than the tails, the attractive interactions of the tails cause them to tilt. This may involve a distortion of the lattice; the surface per rod A occupied by the monolayer increases, which is in turn penalized by the surface tension Σ and the surface pressure Π.

Such considerations lead to the free energy *ansatz*

$$F = V\,\frac{1}{2\kappa}(\frac{V_0}{V} - 1)^2 + (\Sigma + \Pi)A \tag{2}$$

with the volume compressibility of the rods κ and the volume per rod V. The

repulsive interactions between the rods cause additional constraints

$$\text{(i)} \quad \begin{aligned} a &\gtrsim r_t \\ a\cos\theta &\gtrsim r_t \end{aligned} \qquad \text{(ii)} \quad \begin{aligned} (a^2+b^2\cos^2\theta)/4 &\gtrsim r_t^2 \qquad &\text{(NNN)} \\ (a^2\cos^2\theta+b^2)/4 &\gtrsim r_t^2 \qquad &\text{(NN)} \end{aligned} \tag{3}$$

where θ is the tilt angle. It is convenient to define the mismatch parameter $\delta = 1 - r_h/r_t$, and to rewrite the free energy as

$$F \quad \propto \quad \tilde{F} \equiv \Lambda(\sqrt{\frac{V_0}{V}} - \sqrt{\frac{V}{V_0}})^2 + \frac{LA}{V_0} \qquad \text{with} \qquad \Lambda = \frac{L}{2\kappa(\Sigma+\Pi)}. \tag{4}$$

Our task is to minimize $\tilde{F}$ with respect to the surface $A = ab/2$ and volume $V = AL\cos\theta > V_0$, under the constraints (1) and (3). The remaining independent model parameters are Λ and δ. Assuming that $k = \Lambda\delta$ is of order unity or less, the minimum value of $\tilde{F}$ can be expanded in powers of δ. Details of the calculation are presented in the appendix.

In layers with rods tilted towards next nearest neighbors, the volume per rod cannot be optimized, because the distance to the neighbors (i) is too large, $a > r_h > r_t$. The free energy is minimized at $A = \sqrt{3}r_h^2$ and takes the value

$$\tilde{F}_{NNN} = 1 + (2 + \frac{4}{9}k)\delta + (1 - \frac{28}{27}k)\delta^2 + \cdots \tag{5}$$

The head lattice is not distorted. This is an effect of the "hard" constraints of eqn (1), i.e. the hard core interactions between heads. If the heads interact via a softer potential, the lattice gets slightly distorted in the direction of the tilt.

In layers with rods tilted towards nearest neighbors, the volume per rod can be optimized, but at the cost of an increased surface energy. Surface and volume contributions have to be balanced. For large k, $k \gg 1$, the volume

term determines most of the behavior, and one gets

$$\tilde{F}_{NN} \stackrel{k \gtrless 1}{=} \begin{cases} 1 + 4\delta - 6\delta^2 + \cdots & : \quad \delta > \delta_0 \quad \text{(a)} \\ 1 + (4 - 1/k)\delta - (6 - 16/k + 10/k^2)\delta^2 + \cdots & : \quad \delta < \delta_0 \quad \text{(b)} \end{cases} \tag{6}$$

with $\delta_0 = \sqrt{3/2} - 1 = 0.225$. In this case, the head lattice is distorted, and the volume per rod is minimal ($V = V_0$) in the limit $k \to \infty$ or $\delta > \delta_0$. For small k on the other hand, $k \ll 1$, the surface term dominates. The heads form an undistorted lattice, and the free energy is given by

$$\tilde{F}_{NN} \stackrel{k \ll 1}{=} 1 + (2 + k)\delta + (1 - k)\delta^2 + \cdots \tag{7}$$

In the intermediate regime, $k \sim 1$, the smaller of the two solutions (6) or (7) applies. Note that the free energy (7) is always larger than (5). Hence rods tilt towards next nearest neighbors at $k \ll 1$, or generally if distortions of the head lattice are not allowed.

Suppose now that Λ is kept fixed, and the head size is gradually increased. Rods with small heads, $\delta < \delta_{c1} = 0$, are untilted. If the heads are just slightly larger than the tails, $0 < \delta < 1/\Lambda$, the case $k < 1$ applies, and the rods tilt towards their next nearest neighbors. On increasing the head size (and if Λ is sufficiently large), a swiveling transition to a phase with tilt towards nearest neighbors takes place. The transition point δ_{c2} is located by equating eqn (6) with eqn (5). One thus gets a sequence of phase transitions at

$$\delta_{c1} = 0 \quad \text{and} \quad \delta_{c2} = k_c/\Lambda \quad \text{with} \quad k_c = 3.93 \tag{8}$$

to lowest order of δ ($\Lambda > k_c/\delta_0$). Note that the transition at δ_{c1} from the untilted to the tilted state, does not depend on Λ. This is again a consequence of the hard core interactions between the heads. If the heads are soft, they are squeezed together at high pressures (*i.e.*, small Λ), and the rods stand up. Note

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also that the free energy (2) is temperature dependent *via* the temperature dependence of the compressibility κ and the surface tension Σ. However, the model cannot be expected to reproduce thermal properties of a monolayer, since the hard core interactions between the heads are basically athermal.

3 Exact Ground State Calculations.

In order to test these predictions, we have studied numerically the ground state of a system of rods with Lennard-Jones interactions between tails and repulsive soft core interactions between heads. The interaction energy of two rods at grafting distance $\vec{r}$, with tilt direction $\vec{e}_L$, is given by

$$E(\vec{r}, \vec{e}_L) = \int_0^L \int_0^L dl \, dl' \, V_{LJ}(d) + V_h(r), \qquad (9)$$

where d is the distance between elements dl and dl' on the rods, $d = |\vec{r} + (l - l')\vec{e}_L|$, and the potentials are taken to be

$$V_{LJ}(d) = \begin{cases} d^{-12} - 2d^{-6} + 0.031 & : \quad d \leq 2 \\ 0 & : \quad d > 2 \end{cases} \qquad (10)$$

$$V_h(r) = \begin{cases} (\sigma/r)^{12} - 2(\sigma/r)^6 + 1 & : \quad r \leq \sigma \\ 0 & : \quad r > \sigma \end{cases} \qquad (11)$$

The potentials V_{LJ} and V_h are cut at $d = 2$ and $r = \sigma$, respectively, in order to make the problem more tractable. The total energy E_t is the sum over all nonzero pair interactions, *i.e.*, the interactions of a rod with up to 24 pairs [6]. It is minimized with fixed molecular area A by numerical methods. The surface pressure is obtained using $\Pi = -dE_{t,min}/dA$.

The lattice constant and the compressibility of a system of infinitely long rods can be calculated analytically. We identify these parameters with the rod diameter r_t and the volume compressibility κ ($r_t = 0.9333$ and $\kappa = 0,0184$),

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and σ with the head size r_h. This allows a quantitative comparison of the numerical results with the predictions of the previous section.

The phase diagram for chain length $L = 5$ is shown in Figure 3. With increasing head size, one finds the sequence of phases predicted in section 1: Untilted (U), Tilt towards next nearest neighbors (NNN) and towards nearest neighbors (NN). Due to the soft core interactions between the heads, the first transition U-NNN becomes pressure dependent. Apart from this detail, the results are in qualitative and reasonable quantitative agreement with the predictions of eqn (8).

4 Discussion.

In sum, we find that tilt order can be induced in systems of rods with grafted heads by a mismatch of head size and rod diameter. Rods with large heads tilt towards nearest neighbors, and rods with heads just slightly larger than the rod diameter tilt towards next nearest neighbors. The critical head size, at which the swiveling transition occurs, increases with pressure and decreases with the rod length. If distortions of the hexagonal head lattice are not allowed, rods always tilt towards their next nearest neighbors.

This is in agreement with previous theoretical predictions. Scheringer et al [7] report that rods grafted on an undistorted hexagonal lattice tilt towards next nearest neighbors. Kaganer et al [8] find that this remains true, even if one allows for lattice distortions, in systems of pure rods (no heads) which are forced to tilt by the constraint of a fixed homogeneous surface density (see also [10]). Some authors study the effect that tilt towards nearest neighbors can be induced by additional, attractive interactions between the rods and the surface

[8, 9]. The present work indicates that it might simply be a consequence of the larger head group size.

Our effect offers a simple explanation for the observations of Shih et al [3] and Fischer et al [4], discussed in the introduction. It also provides an interpretation for earlier experimental findings. In particular, the fact that phases with tilt towards next nearest neighbors appear at high surface pressures (see Figure 1), comes out quite naturally.

Shih et al [11] have studied monolayers of heneicosanic acid in the presence of calcium ions in the subphase, and systematically varied the pH of the subphase. At low pH, they find a sequence of phases with tilt towards nearest neighbors, tilt towards next nearest neighbors, and no tilt, as a function of pressure. On increasing the pH, the phase tilted towards next nearest neighbors moves down to lower pressures, and finally replaces the phase with tilt towards nearest neighbors. At even higher pH, the monolayer is untilted at all pressures. Assuming that the effective size of the $COOH^-$ head groups is reduced at high pH – *e.g.*, due to more efficient screening of the electrostatic interactions at higher concentration of positive ions in the subphase – this result corresponds exactly to the predictions of our model.

To conclude, our simple considerations provide an explanation for a remarkable variety of experimental observations. Obviously, the real interactions between head groups in Langmuir monolayers are much more complicated than those assumed here. Nevertheless, the success of our model suggests that the influence of head groups on the microscopic structure of Langmuir monolayers is to a large extent simply determined by their size.

Acknowledgement.

Appendix

We wish to minimize the free energy (2) with the constraints (1) and (3). For tilt towards next nearest neighbors, the solution can be written down immediately: $a = r_h$, $b = \sqrt{3}r_h$, $\cos\theta = \sqrt{(4 - (1+\delta))^2)/3(1+\delta)^2}$, and

$$\tilde{F}_{NNN} = (1+\delta)^2 + \Lambda\left(\frac{3 + 4(1+\delta)^2 - (1+\delta)^4}{\sqrt{3}(1+\delta)\sqrt{4 - (1+\delta)^2}} - 2\right) \tag{12}$$

The expansion of $\tilde{F}_{NNN}$ in powers of δ yields (5).

For tilt towards nearest neighbors, different solutions are possible. If the volume term dominates, one achieves $V = V_0$ with $\cos\theta = r_t/a$, $b = \sqrt{3}r_t$ and minimizes the surface A under this constraint with $a/r_t = \sqrt{4(1+\delta)^2 - 3}$.

$$\tilde{F}_{NN}^{(V)} = \sqrt{4(1+\delta)^2 - 3}. \tag{13}$$

In this case, the head lattice is distorted. Expansion of $\tilde{F}_{NN}^{(V)}$ gives (6.a).

If the surface term dominates, the head lattice is not distorted, ($b = \sqrt{3}r_h$, $a = r_h$) and with this constraint the volume is minimal for $\cos\theta = r_t/a$.

$$\tilde{F}_{NN}^{(A)} = (1+\delta)^2 + \Lambda\frac{\delta^2}{(1+\delta)} \tag{14}$$

Expansion yields (7).

If none of the two terms dominates, the solution lies between (13) and (14): $b = \sqrt{3}r_t y$ and $a/r_t = \sqrt{4(1+\delta)^2 - 3y^2}$ with $1 < y < 1+\delta$ ($\cos\theta = r_t/a$).

$$\tilde{F}_{NN} = \min_{1<y<1+\delta} \mathcal{F}(y) \quad \text{with} \quad \mathcal{F}(y) = y\sqrt{4(1+\delta)^2 - 3y^2} + \Lambda\frac{(y-1)^2}{y} \tag{15}$$

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Note that $d\mathcal{F}/dy|_{y=1} \gtrless 0$ for $\delta \gtrless \delta_0 = \sqrt{3/2} - 1$. If $\delta > \delta_0$, δ_0, the function $\mathcal{F}(y)$ has no minimum in the interval $]1, 1 + \delta[$, and $\tilde{F}_{NN}$ is either given by $\mathcal{F}(1) = \tilde{F}_{NN}^{(A)}$, or $\mathcal{F}(1+\delta) = \tilde{F}_{NN}^{(V)}$. If $\delta < \delta_0$, $\mathcal{F}(y)$ has a minimum. The surface term still dominates at small Λ ($\Lambda \lesssim 1/\delta$), $\tilde{F}_{NN} = \tilde{F}_{NN}^{(A)}$. At larger Λ, no closed expression for $\tilde{F}_{NN}$ can be given, but an expansion in powers of δ is possible: The minimum of $\mathcal{F}(y)$ is found at $y = 1 + \alpha\delta$ with

$$\alpha = \frac{1}{k} + \frac{21 - 16k}{2k^2}\delta + \frac{4(40 - 42k + 9k^2)}{k^3}\delta^2 + \cdots \tag{16}$$

$(k = \Lambda\delta)$, which leads to eqn (6.b).

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Figure Captions

Figure 1: Part of the generic phase diagram for fatty acid monolayers. Solid lines are first order transitions, broken lines are second order. The amphiphile molecules are tilted towards next nearest neighbors in the phases Ov and L'_2, towards nearest neighbors in L_{2d} and L_{2h}, and untilted in S and LS. In the S, L'_2 and L_{2h} phases, the backbones of the chains are ordered, the other phases are rotator phases. Increasing the length of the aliphatic chains shifts the phase diagram to higher temperatures (after [2]).

Figure 2: Side view of the rigid rod model (top) and top view of the head lattice (bottom). We consider tilt directions in the direction of a (nearest neighbors), or b (next nearest neighbors. (i) and (ii) mark the different types of direct neighbors in this geometry.

Figure 3: Ground state phase diagram of the model of section 3 (rods with Lennard-Jones interactions) in the plane of head size σ vs pressure Π, at rod length $L = 5$. Phases are: tilt towards next nearest neighbors (NNN), towards nearest neighbors (NN), untilted (U). Dashed lines indicate the prediction of eqn (8) with $\Sigma = 6.7$.
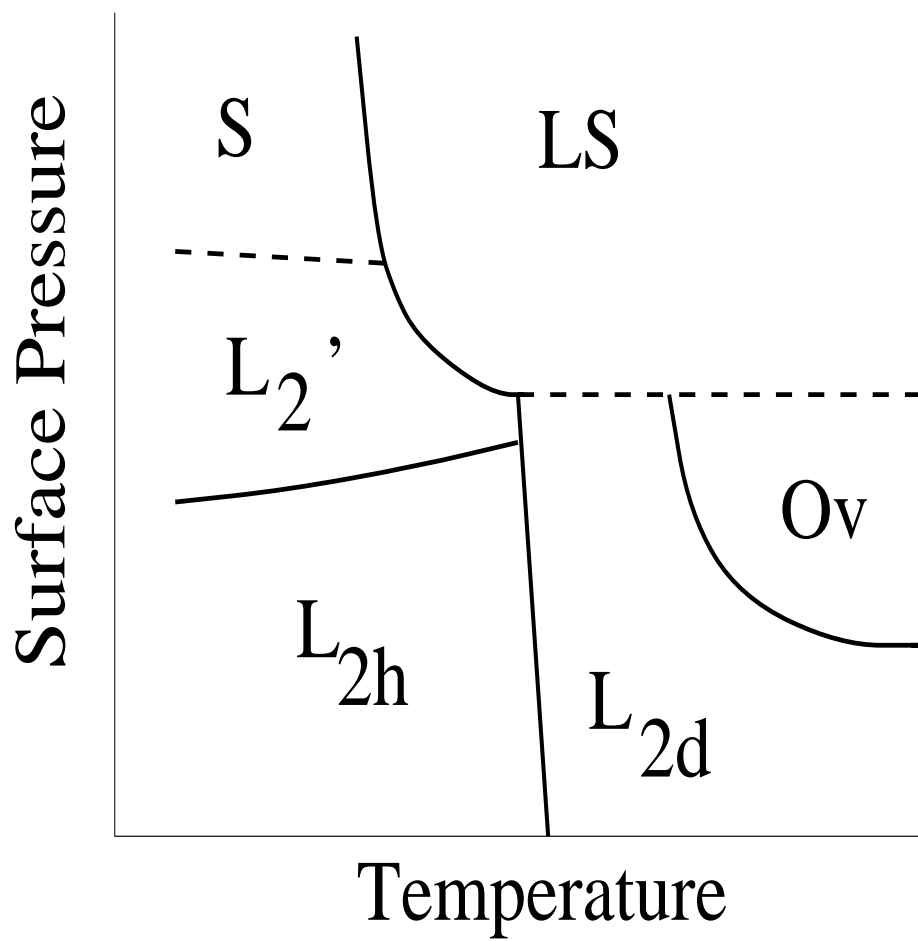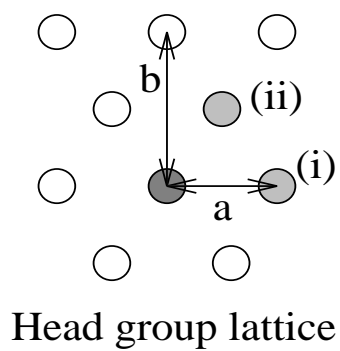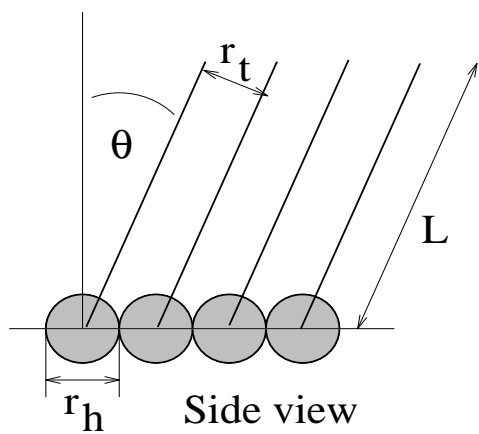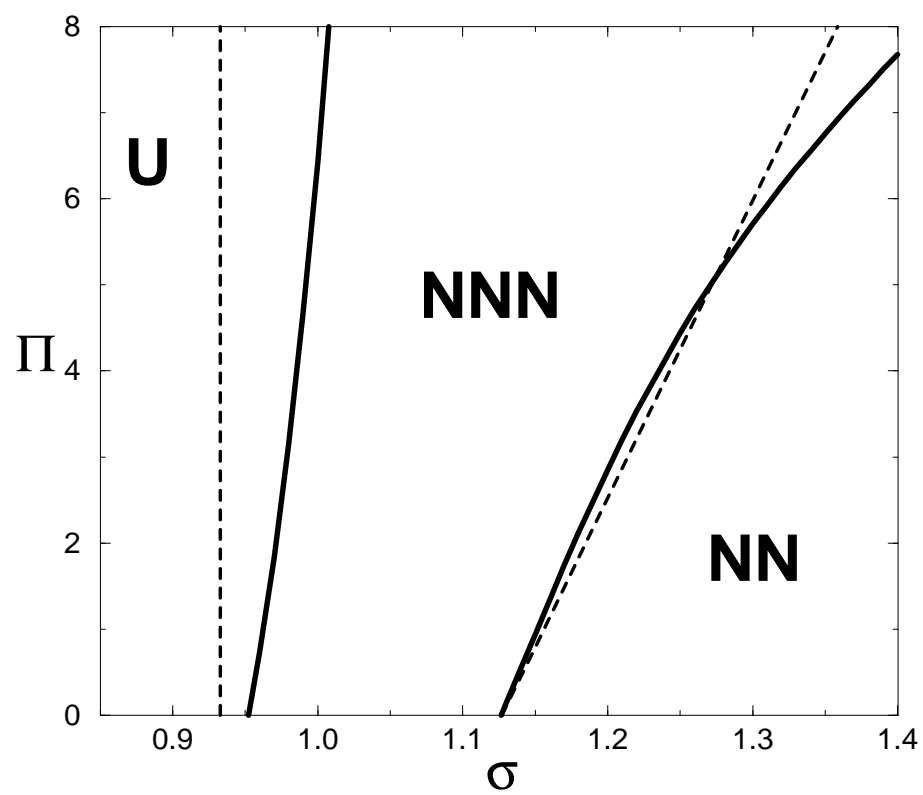
Figure 1
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Side view

Head group lattice

Figure 3
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